

# **CORRELATION OF LIQUID VISCOSITY AT THE NORMAL BOILING POINT<sup>1</sup>**

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## ABSTRACT

The importance of liquid viscosity in chemical process design makes it one of the most measured transport properties. Nevertheless, of the 1893 compounds in the DIPPR 801 pure-component database, liquid viscosity and its temperature dependence (at 1 atm) have been predicted for nearly 50% of the compounds because no experimental data are available. Unfortunately, prediction methods for liquid viscosity often fail significantly, particularly near the normal boiling point. Moreover, experimental data measured at lower temperatures are often extrapolated to higher temperatures with erroneous results. To improve liquid viscosity prediction and extrapolation of experimental data to higher temperatures, we propose an empirical rule for estimating the viscosity of organic compounds at their normal boiling point,  $\eta_{\text{Lb}}$ . The proposed rule, developed and validated with the available experimental data in the DIPPR 801 database, was applied as a quality control check on the 1893 compounds in the database and was found to improve the available temperature dependent viscosity correlation in the database for 250 compounds. Of particular significance is a smooth trend within chemical families for the value of the viscosity at the normal boiling point.

**KEY WORDS:** correlation; data; empirical rule; extrapolation; liquid; normal boiling point; prediction; viscosity

## 1. INTRODUCTION

The importance of liquid viscosity in chemical process design makes it one of the most measured transport properties. Liquid viscosity has a direct and large effect on heat transfer coefficients, which are especially important for heat exchangers and various other heat transfer considerations, and are also somewhat important in distillation calculations. Viscosity is also of extreme importance for calculating pressure drops, as for pump and piping calculations. Nevertheless, the DIPPR 801 database – one of the world’s premier databases for physical property data for chemical engineering applications – still contains predicted liquid viscosity data for nearly 50% of the compounds in the database, due to a lack of available experimental data.

While many prediction methods for liquid viscosity ( $\eta_L$ ) have been developed over the years, Poling, Prausnitz, and O’Connell point out that “little theory has been shown to be applicable to estimating liquid viscosities”<sup>1</sup>. Therefore, most estimation methods are empirical in nature. We have found that often these methods fail significantly, particularly near the normal boiling point. Moreover, experimental data measured at lower temperatures are often extrapolated to higher temperatures with erroneous results.

To improve liquid viscosity prediction and extrapolation of experimental data to higher temperatures, we propose an empirical rule for estimating the viscosity of organic compounds at their normal boiling point,  $\eta_{Lb}$ . The purpose of this paper is to present this empirical rule and its historical background; to document the rule’s validity and wide-ranging applicability; to demonstrate the surprising variety of ways in which the rule has been found to be useful for improving the liquid viscosity correlations in the DIPPR 801 database; and to propose the use of the rule as a starting point for developing a quantitative structure-property relationship (QSPR) correlation for liquid viscosity.

## 2. THE EMPIRICAL RULE

The empirical rule, in its simplest form, is as follows: For most organic liquids, the liquid viscosity at the compound’s normal boiling point,  $\eta_{Lb}$ , should fall within the range of 0.15 to 0.55 cP; standard methods available for establishing the rest of the viscosity-versus-temperature curve can then be used to obtain viscosities at other temperatures, providing that they are consistent with this empirical rule. (Note that 1 cP = 1 centipoise = 0.001 Pa · s = 1 mPa · s.)

Recent work within DIPPR Project 801 has shown that this rather simple-looking empirical rule is remarkably powerful in practice, essentially serving as a “missing link” between the regression, extrapolation, prediction, and evaluation of liquid viscosity data for organic compounds, as we will demonstrate.

### 3. HISTORICAL BACKGROUND AND VALIDATION

The idea of using the liquid viscosity at the normal boiling point ( $\eta_{Lb}$ ) as a correlating parameter for liquid viscosity data is not a new one; in fact, its use can be traced at least as far back as 1918, when, according to Partington<sup>2</sup>, Arrhenius suggested the relation

$$\eta_{Lb} = C\sqrt{\rho_{Lb}} \quad (1)$$

and reported that the constant C varied from 0.23 to 0.32, where  $\eta_{Lb}$  is the liquid viscosity at the normal boiling point (in cP) and  $\rho_{Lb}$  is the liquid density at the normal boiling point (in g/cm<sup>3</sup>). Note that if one utilizes the fact that  $\rho_{Lb}$  generally falls within the range of 0.6 to 1.3 g/cm<sup>3</sup> for most organic liquids, then it is seen that Arrhenius' equation would typically yield  $\eta_{Lb}$  values in the range of 0.18 to 0.36 cP. (Gambill<sup>3</sup> later proposed the use of an average value for C of 0.275, which would yield  $\eta_{Lb}$  values in the slightly narrower range of 0.21 to 0.31 cP.)

Some 25 years after Arrhenius, Friend and Hargreaves<sup>4</sup> proposed the "rheochor" method for estimating  $\eta_{Lb}$ . The rheochor method is a group-contribution method which correlates  $\eta_{Lb}$  with both  $\rho_{Lb}$  and a "rheochor" term determined from the summation of atomic-group contributions based on the atomic groups present in the compound's molecular structure.

In 1959, Gambill<sup>3</sup>, after reviewing the earlier correlations of Arrhenius and Friend and Hargreaves, proposed two simplifications. Gambill's first simplification was mentioned earlier: the use of an average value for C of 0.275 in Arrhenius' equation. Gambill's second simplification went one step further, saying that one could assume that  $\eta_{Lb} = 0.29$  cP for all organic compounds, and that the accuracy of this assumption would usually still be suitable for most engineering calculations.

Grain<sup>5</sup> later proposed that, instead of using the historical methods described above for obtaining a value for  $\eta_{Lb}$ , one could use the following categorizations for  $\eta_{Lb}$ :

- Alcohols (aliphatic and aromatic):  $\eta_{Lb} = 0.45$  cP
- Primary amines (aliphatic and aromatic):  $\eta_{Lb} = 0.45$  cP
- All other organic liquids:  $\eta_{Lb} = 0.2$  cP\*

\*Exceptions: benzene (use 0.3 cP) and cyclohexane (use 0.4 cP)

Grain's categorizations, however, appear to be of questionable validity; an examination of the experimentally-derived  $\eta_{Lb}$  values in Table I and Figure 1 shows that there is probably as much variation in the  $\eta_{Lb}$  values within one of Grain's categories as there is between the different categories. For example, from the alcohol curve in Figure 1, it is seen that Grain's assumption of an  $\eta_{Lb}$  value of 0.45 cP is a reasonable assumption for alcohols such as ethanol, propanol, phenol, and maybe butanol, but the 0.45 cP assumption gets progressively worse at higher carbon numbers; one would be better off to assume a much lower value, on average, if one were considering a wider range of alcohols. Similarly, Grain's value of 0.45 cP for amines seems to be unwarranted, and 0.2 cP for "all other

organic liquids” seems to be a little low overall. It would appear that Grain’s categorizations were most likely based on a very limited set of compounds – covering perhaps only a few of the most common organic compounds in each category – such that Grain’s recommended values are neither as valid nor as discriminating as they purport to be. Therefore, Grain’s categorizations are not recommended for general use.

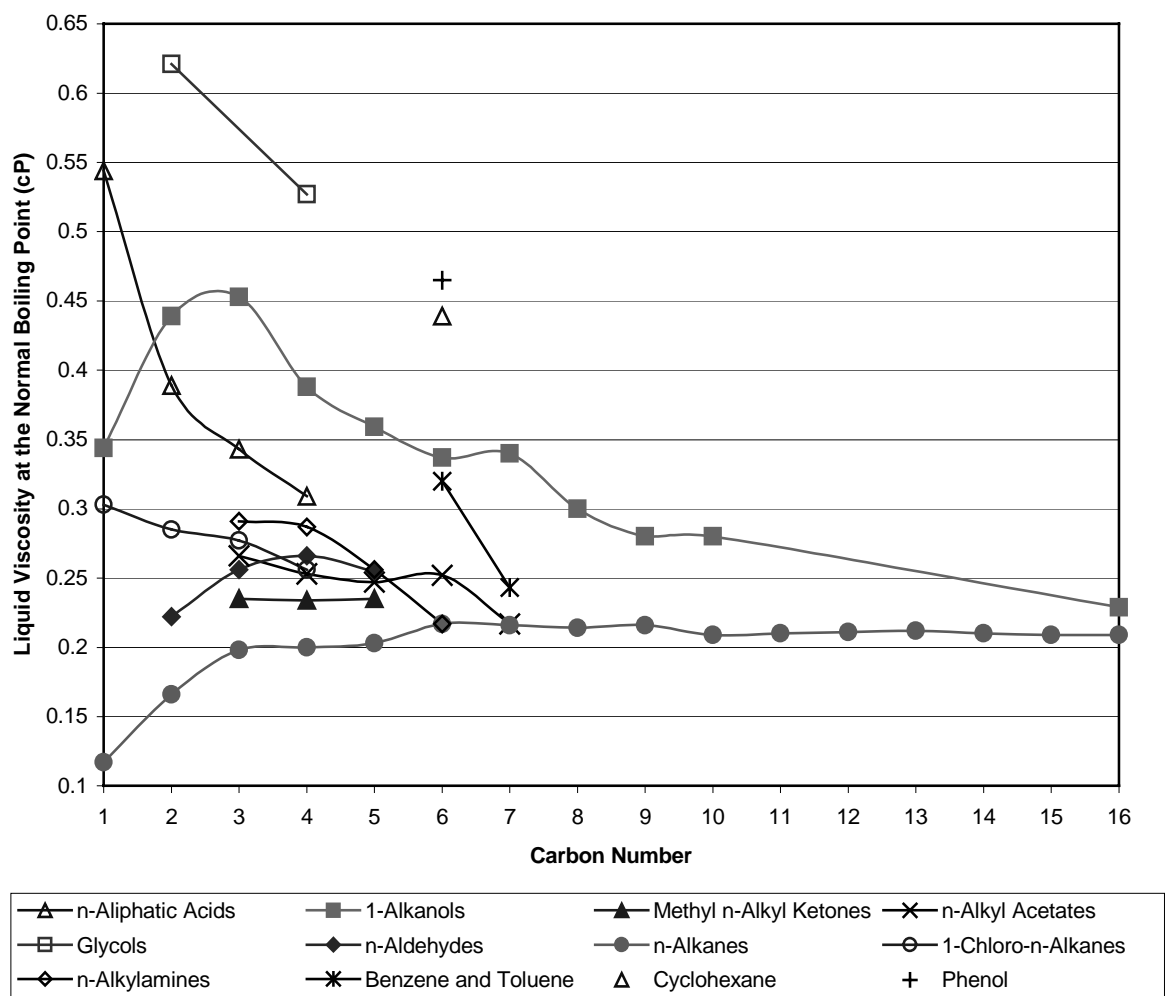
**Table I. Comparison of the Rheochor Method, Gambill's Constant-Value Method, and Grain's Method**

	Liquid Viscosity at the Normal Boiling Point (cP)			
	(Exp'l)	Rheochor	Gambill	Grain
methane	0.117	0.053	0.29	0.2
propane	0.198	0.280	0.29	0.2
heptane	0.216	0.208	0.29	0.2
ethylene	0.165	0.074	0.29	0.2
cyclohexane	0.439	0.494	0.29	0.4
cyclohexene	0.332	0.430	0.29	0.4
benzene	0.320	0.232	0.29	0.3
diphenyl	0.257	0.225	0.29	0.3
acetone	0.235	0.202	0.29	0.2
methyl ethyl ketone	0.234	0.234	0.29	0.2
acetaldehyde	0.222	0.173	0.29	0.2
methanol	0.344	0.527	0.29	0.45
propanol	0.453	0.494	0.29	0.45
phenol	0.465	0.524	0.29	0.45
p-cresol	0.352	0.468	0.29	0.45
acetic acid	0.389	0.364	0.29	0.2
propionic acid	0.343	0.323	0.29	0.2
ethyl acetate	0.253	0.494	0.29	0.2
amyl acetate	0.217	0.208	0.29	0.2
phenyl n-propyl ether*	0.244	0.211	0.29	0.2
carbon tetrachloride	0.483	0.418	0.29	0.2
chlorobenzene	0.286	0.251	0.29	0.3
hydrogen chloride*	0.458	0.488	0.29	0.2
p-dichlorobenzene	0.304	0.283	0.29	0.3
n-butyl bromide	0.310	0.303	0.29	0.2
acetonitrile	0.270	0.197	0.29	0.2
diethylamine	0.227	0.213	0.29	0.45
methyl aniline	0.287	0.272	0.29	0.45
dimethyl aniline	0.263	0.237	0.29	0.45
nitromethane	0.308	0.300	0.29	0.2
nitro-n-pentane*	0.250	0.230	0.29	0.2
ethyl nitrite*	0.228	0.205	0.29	0.2
n-amyl nitrite*	0.239	0.222	0.29	0.2
Average absolute error (%):		18.9	26.4	26.8

\*An experimental value not available in DIPPR database; value is from Reid and Sherwood (Table 6-8, p. 214).

Source of experimental data: DIPPR Project 801 database, sponsors' January 2003 version (unless otherwise noted).

Rheochor method values are taken directly from Reid and Sherwood's Table 6-8.



**Figure 1. Liquid Viscosity at the Normal Boiling Point vs. Carbon Number**

Table I provides a comparison of three of the historical methods involving  $\eta_{\text{Lb}}$ : the rheochor method, Gambill's 0.29-cP assumption, and Grain's categorization method. Table I shows that, at least for the given set of compounds (a set chosen to include representatives of the most common families of organic compounds), the rheochor method is the best of the three methods, while Gambill's and Grain's methods are practically of equal accuracy. (Choosing other  $\eta_{\text{Lb}}$  values for the "all the same" assumption, it is found that the average absolute error is minimized at 23.2% when  $\eta_{\text{Lb}} = 0.25$  cP.)

Despite the long-standing history of correlations involving  $\eta_{\text{Lb}}$ , the idea of using  $\eta_{\text{Lb}}$  as a correlating parameter for estimating liquid viscosity data seems to have fallen into obscurity in recent decades. For example, after being prominently featured in the first edition of the book by Reid and Sherwood<sup>6</sup>, the idea was only obliquely mentioned in the third edition of the book<sup>7</sup> and not mentioned at all in the fourth and fifth editions.<sup>1,8</sup> Furthermore, when the first author of the present paper described to other participants in a recent Design Institute for Physical Properties (DIPPR) meeting how an empirical rule involving  $\eta_{\text{Lb}}$  was a useful tool for evaluating and estimating LVS data, it appeared from the reaction of the participants (most of whom were physical property experts) that the idea was a mostly unfamiliar one.

Some additional observations from Table I and Figure 1:

- Table I and Figure 1 clearly show the validity and general universality of the proposed empirical rule.
- In general, compounds with greater hydrogen bonding have the highest  $\eta_{\text{Lb}}$  values, while the alkanes have the lowest  $\eta_{\text{Lb}}$  values.
- Out of all of the compounds covered in Table I and Figure 1, only methane and ethylene glycol fall outside the 0.15-0.55 cP range of the proposed empirical rule.
- If the rule is tightened to the slightly narrower range of 0.2 to 0.5 cP, the outliers are the low-boiling compounds methane, ethane, ethylene, and propane on the low end, and the highly hydrogen-bonded compounds formic acid, ethylene glycol, and 1,4-butanediol on the high end.
- There is an interesting overall trend of  $\eta_{\text{Lb}}$  values decreasing with increasing carbon number within a given family of compounds. In fact, many families appear to be asymptotically approaching a value of about 0.22 cP as carbon number increases.

The first author of the present paper, and others at Eastman Chemical Company, have been using the proposed empirical rule (or slight variations of it) for many years and have found it to be quite useful. Since being brought to the attention of DIPPR, the empirical rule has been further investigated and validated using the DIPPR 801 database, and the rule has proved useful from several different standpoints in the work of DIPPR Project 801, as is detailed in Section 5.



#### 4. APPLICABILITY OF THE EMPIRICAL RULE

The proposed empirical rule is presently recommended mainly for organic compounds containing carbon, hydrogen, oxygen, nitrogen, and chlorine. However, Table I also includes some organic compounds containing bromine which also obey the rule. Additional preliminary investigations by the authors have found the rule to also be applicable to other types of compounds – including, surprisingly, even some inorganic compounds, such as phosphine (0.20 cP), water (0.28 cP), and sulfur dioxide (0.43 cP). The fact that the rule appears to be applicable to glycol ethers suggests that the rule is valid for multifunctional compounds (compounds containing more than one functional group) in addition to monofunctional compounds, although this should be studied further. Several brominated and/or fluorinated organic compounds have been found to have  $\eta_{Lb}$  values slightly higher than the rule's range, falling typically in the range of 0.5 to 0.6 cP.

#### 5. USE OF THE EMPIRICAL RULE TO IMPROVE THE DIPPR 801 DATABASE

New compounds included in the DIPPR 801 database must satisfy 28 quality control checks designed to ensure that properties for the compound are thermodynamically consistent, reasonable, and satisfy known trends and relationships. In the past, no quality control check was available for liquid viscosity ( $\eta_{Lb}$ , or LVS). We have recently implemented the  $\eta_{Lb}$  rule as an additional quality control check and have examined the DIPPR recommended correlations for  $\eta_L$  for all compounds in the database using the rule. The check produced 401 compounds out of 1800 that failed the  $\eta_{Lb}$  criterion.

We have reviewed the raw data and DIPPR correlations for all 401 compounds that failed the quality control check. In 151 cases, no change was made in the correlation, either because sufficient quality experimental data were available to classify these compounds as exceptions to the  $\eta_{Lb}$  rule or because no better values could be obtained from the limited data available. Changes were made in the other 250 cases as guided by the rule. Requiring the value of the viscosity to satisfy the rule often made significant improvements in the viscosity correlation and assisted us in evaluating conflicting experimental data sets. The kinds of improvements made in the database correlation for liquid viscosity by use of the  $\eta_{Lb}$  rule can be grouped into four categories.

##### 5.1. Improved correlation and temperature range

The  $\eta_{Lb}$  rule aided the regression of the DIPPR liquid viscosity correlation for a large number of compounds. In many cases, the correlation had been developed from data at temperatures much lower than the normal boiling point and extrapolation of the correlation to higher temperatures produced values that failed the  $\eta_{Lb}$  test. The  $\eta_{Lb}$  rule allowed improved correlation of the liquid viscosity data with appropriate extrapolation to higher temperatures. Examples of this kind of improvement are shown in Figures 2 and 3 for *n*-heptylbenzene and nonylphenol, respectively. Note in Figure 2 that although there is considerable experimental data for temperatures below the normal boiling point (NBP) for

this compound, extrapolation to the NBP with the previous regression produced a value that did not satisfy the quality control test. The improved regression satisfies the test and extrapolates reasonably to the critical temperature. In Figure 3, the minimum in the previous correlation was eliminated by addition of the  $\eta_{Lb}$  criterion.

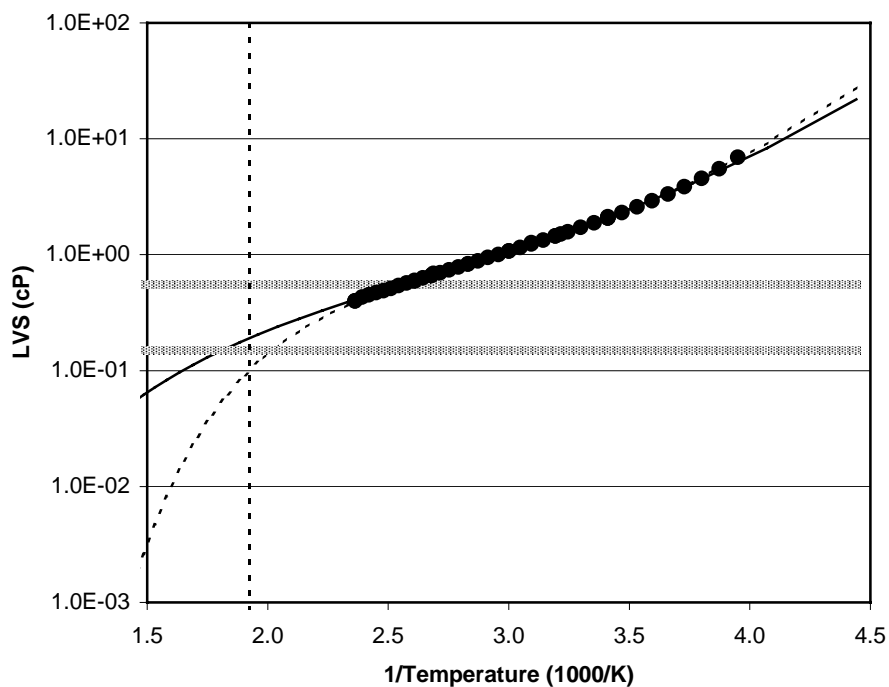


Figure 2.  $\eta_L$  for *n*-heptylbenzene with accepted experimental data (●), the previous DIPPR correlation (- - -), and the revised correlation (—). The vertical dotted line is at the NBP and the horizontal lines show the  $\eta_{Lb}$  rule.

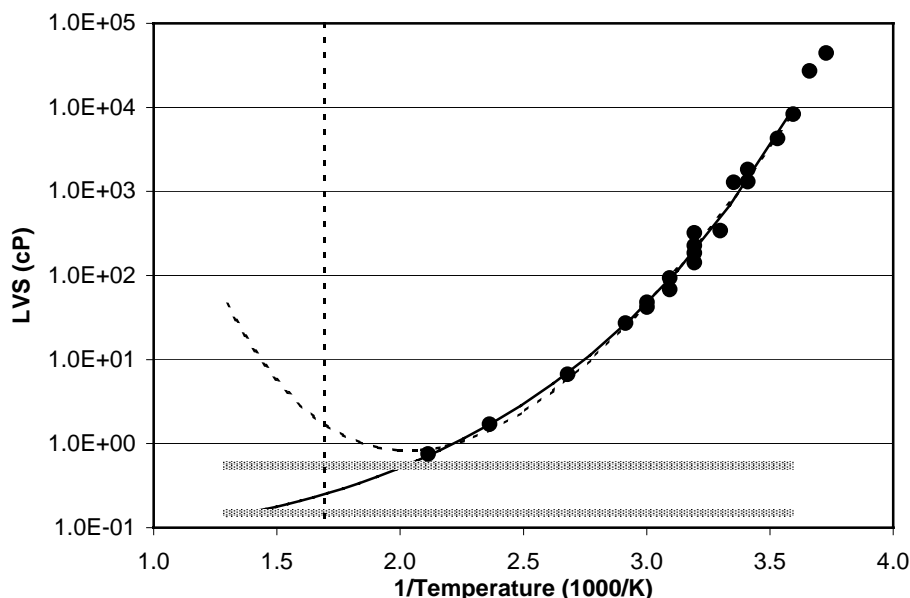


Figure 3.  $\eta_L$  for nonylphenol with accepted experimental data (●), the previous DIPPR correlation (- - -), and the revised correlation (—). The vertical dotted line is at the NBP and the horizontal lines show the  $\eta_{Lb}$  rule.

In some cases, the number of coefficients used in the DIPPR correlation caused this data range problem, and application of the  $\eta_{Lb}$  rule provided clear evidence of the incorrect regression. In these cases, the slope ( $\ln(\eta_L)$  vs.  $1/T$ ) of the last few points was used to extrapolate  $\eta_L$  to the NBP and a value was obtained consistent with the rule even though the correlation itself failed the quality control check.

## 5.2. Improved evaluation of experimental data sets

Application of the  $\eta_{Lb}$  rule in several cases aided in what we believe is a better evaluation of available experimental data sets. Some data that had been evaluated previously as less accurate or had been rejected altogether were found to be more consistent with the rule than some of the accepted data. Often that evaluation had been based on the relationship of data sets to what was then felt to be the best correlation. An example of this kind of improvement is for the case of *n*-hexylbenzene shown in Figure 4. Note that some higher temperature data that had been previously rejected because of their deviation from the previously used correlation are now deemed acceptable because of their consistency with the rule.

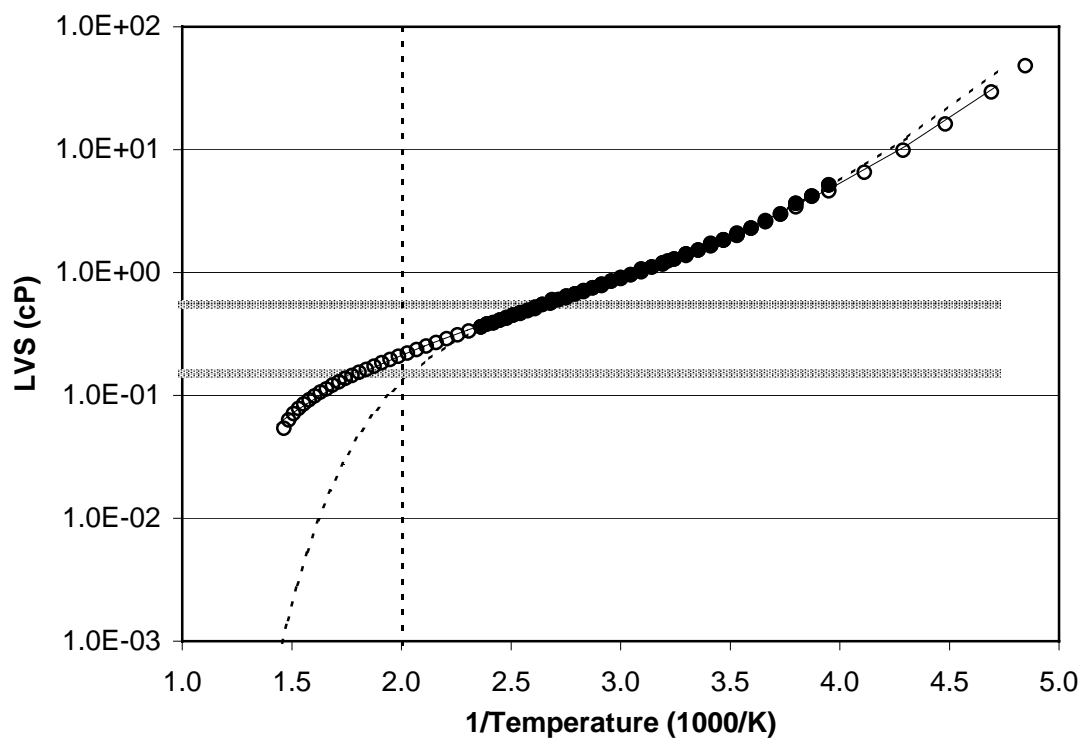


Figure 4.  $\eta_L$  for *n*-hexylbenzene with accepted experimental data (●), previously not used points (○), the previous DIPPR correlation (---), and the revised correlation (—). The vertical dotted line is at the NBP and the horizontal lines show the  $\eta_{Lb}$  rule.

In some cases, data reported in the literature subsequent to the last review of the compound were obtained that agreed with the  $\eta_{Lb}$  rule for compounds that failed the quality control check. For example, shown in Figure 5 is  $\eta_L$  as a function of temperature for 1,6-hexanediol. In this case, no previous  $\eta_L$  data were available and the van Velzen<sup>9</sup> method had been used to predict the values. As can be seen, the predicted values failed the  $\eta_{Lb}$  test, but the experimental data of Lech et al.<sup>10</sup> and Bleazard et al.<sup>11</sup> have since been added to the database and they are consistent with our new quality control check.

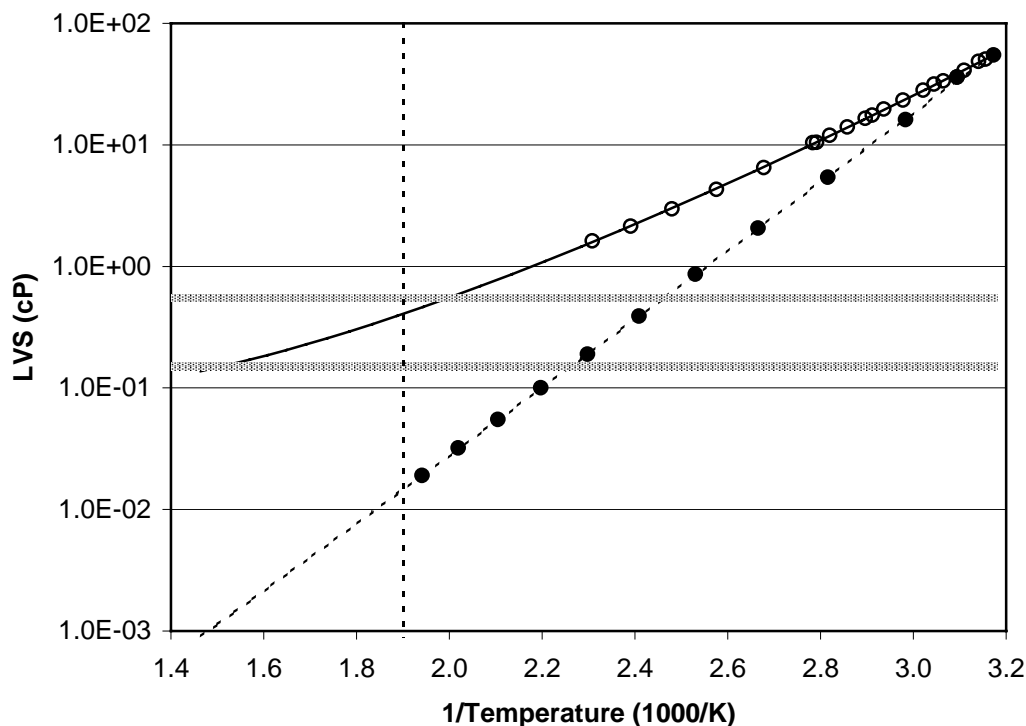
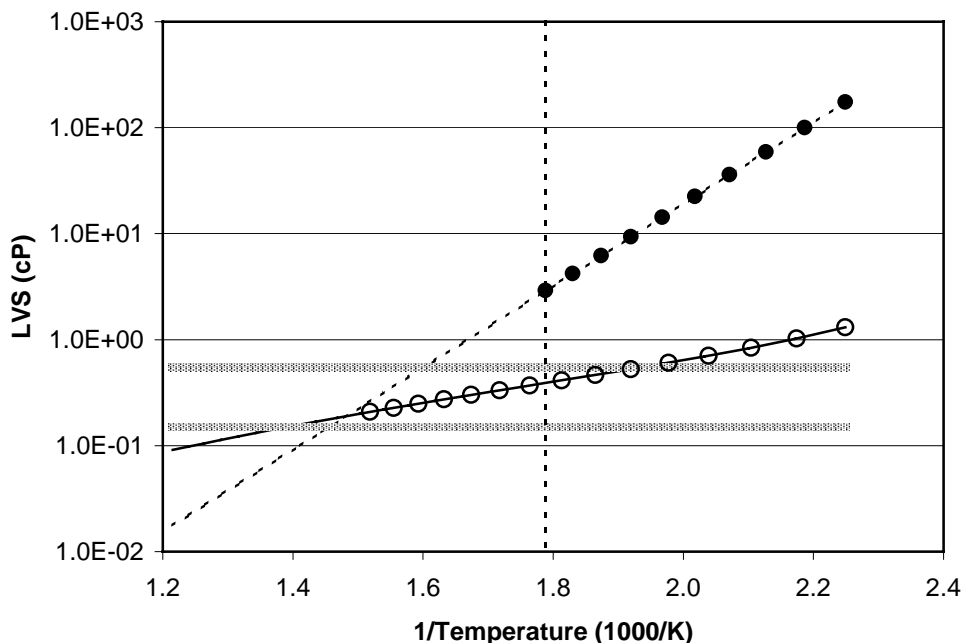


Figure 5.  $\eta_L$  for 1,6-hexanediol with previously estimated data (●), recent experimental data (○), the previous DIPPR correlation (---), and the revised correlation (—). The vertical dotted line is at the NBP and the horizontal lines show the  $\eta_{Lb}$  rule.

### 5.3. Evaluation of predicted values

A hallmark of the DIPPR database is its emphasis on completeness, meaning that when experimental data are unavailable, prediction methods are used to ensure that at least a best estimate is available for all 44 properties for each compound in the database. In several cases,  $\eta_L$  correlations for compounds that failed the  $\eta_{Lb}$  test were based upon predicted data, and the  $\eta_{Lb}$  rule was employed to aid in assessing the reliability of several estimation methods. Interestingly, two of the methods recommended by reviews<sup>1,8</sup> of liquid viscosity correlations, the van Velzen and Bhethanabotla<sup>12</sup> methods, often did not satisfy the  $\eta_{Lb}$  rule. Predictions using these methods for multifunctional compounds often exhibited large variations from the rule. An example of using the  $\eta_{Lb}$  rule to aid in

selecting between competitive prediction methods is illustrated in Figure 6 for *p*-hydroquinone, where we have selected the Przewdziecki-Sridhar<sup>13</sup> estimated values over those obtained from the van Velzen method.



**Figure 6.**  $\eta_L$  for *p*-hydroquinone with van Velzen estimated data (●), Przewdziecki-Sridhar estimated values (○), the previous DIPPR correlation (---), and the revised correlation (—). The vertical dotted line is at the NBP and the horizontal lines show the  $\eta_{Lb}$  rule.

#### 5.4. Improved family trends

As previously discussed, the trend within chemical families of  $\eta_{Lb}$  is compelling evidence of the underlying physics of the rule. These regular trends for  $\eta_{Lb}$  have been used in reverse to improve the quality of the correlations and accepted values in the database. For example, the family trends previously in the database for the *n*-alkane and *n*-alcohol families are shown in Figure 7. When the available  $\eta_L$  data were re-regressed for each individual alcohol using the  $\eta_{Lb}$  criterion to guide the extrapolation of that data to higher temperatures, the smoothed family curve shown in Figure 7 for the alcohols was obtained. There was no degradation of the agreement between the correlation and the experimental data by this procedure; instead, the procedure improved the range over which the correlation was effective while smoothing the family trend.

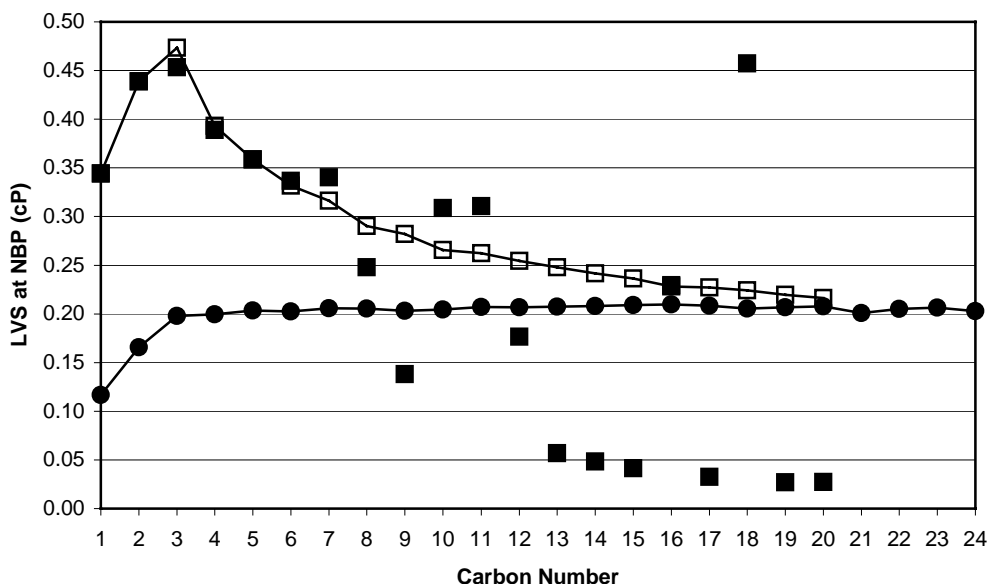


Figure 7.  $\eta_{Lb}$  from the DIPPR database correlations for *n*-alkanes (●, line), the original correlations for *n*-alcohols (■), and the new correlations for *n*-alcohols (□, line).

## 6. CONCLUSION

An empirical rule for estimating the liquid viscosity of organic compounds at their normal boiling point has been developed and validated with the available experimental data in the DIPPR 801 database. The rule is applicable to many different types of organic compounds. Although simple-looking, the rule has been found to be remarkably powerful in practice, providing a valuable link between the regression, extrapolation, prediction, and evaluation of liquid viscosity data. The rule was applied as a quality control check on the complete DIPPR 801 database and was found to improve the available temperature dependent viscosity correlation in the database for 250 compounds. Also, an interesting overall trend of  $\eta_{Lb}$  values decreasing with increasing carbon number within a given family of compounds has been observed; in fact, all families appear to be asymptotically approaching a value of about 0.22 cP as carbon number increases. It is theorized that the molecular descriptors that characterize the electron distribution of molecules may correlate with  $\eta_{Lb}$  values; a quantitative structure-property relationship (QSPR) study is now ongoing at Brigham Young University to further investigate this theory and to attempt to identify a generalized structural-dependence relation for  $\eta_{Lb}$ .

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